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Biosorption of Ammonia from Wastewater using Eichhornia Crassipes Leaves Powder

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Abstract An increasing of ammonia concentration in water is toxic to all forms of aquatic life. The adsorption behavior of a low-cost adsorbent, *Eichhornia Crassipes* leaves powder (ECLP), with respect to ammonia, has been conducted to consider its application for ammonia removing from drainage wastewater. The batch method was considered for ammonia removal to determine the optimum parameters like biosorbent dose ranged between (1-5 g/L), the pH is adjusted in the range between (3 - 9), sampling are taken after contact time (5, 10, 20, 30, 40, 60 minute) with the initial concentration of ammonia of (3, 4, 6, 8, 10 mg/L). 88% maximum removal was achieved at following optimum conditions; pH value = 5, sorbent dose 5 g/L, 10 mg/L initial ammonia concentration for 40 minute contact time. The Langmuir and Freundlich equations were employed to determine the equilibrium isotherms in terms of adsorption affinity and maximum adsorption capacity. The results indicated the Langmuir equation was well fitted the equilibrium adsorption proving monolayer adsorption. On the other hand, *Eichhornia Crassipes* leaves powder was employed to treat a composite sample of real drainage wastewater collected from Sabal drain at Menoufia, Egypt. The maximum removal efficiency of ammonia was reached to 87 % at pH value =7.5, sorbent dose 5 g/L, contact time (40 minute) and initial concentration 7.1 mg/L. Also, *Eichhornia Crassipes* leaves powder was found to be efficient to remove chloride, sulphate, nitrates, nitrite, silica, iron, manganese, copper, zinc, aluminum and lead from real drainage wastewater the sum of total cost of the treatment processes were ranged between 0.48 and 0.55 $/m^3 depending on the concentration of ammonia in the wastewater influents.

Keywords Biosorption; *Eichhornia Crassipes* leaves powder; Ammonia; real drainage wastewater

1. Introduction

Ammonia is the primary form of widespread nitrogen pollution in the hydrosphere. In aqueous solutions, ammonia is a base in nature forming a conjugated pair with the ammonium ion, according to the reversible reaction:

$$NH_3 \leftrightarrow NH_4^+ \quad (1)$$

The reaction pKa is 9.3, at this pH value, the ionized (NH_4^+) and unionized (NH_3) forms are equal at this concentration. But when the pH of the solution is less than 9.3, hydrogen ions attached to ammonia to yield ammonium ions [1]. The concentrations of both NH_3 and NH_4^+ together are referred often to as total ammonia nitrogen. For all vertebrates, ammonia is toxic, causing convulsions, coma and even cell death in the central nervous system [2-4]. At very low ammonia concentration ~ 0.2 mg/L, it caused increasing of oxygen demand in aquatic sources and cause damage to aquatic life and it has toxic effect on human health, the metabolism is influenced by ammonium chloride through shifting the equilibrium of acid-base, disturbing the tolerance of glucose and causing a reduction of the tissue sensitivity to insulin [5, 6].

Many techniques such as biological, chemical and adsorption treatment technologies were used to remove of ammonia from wastewater. Nitrification/Denitrification are biological methods for removing of ammonia from municipal and industrial wastewater, while at elevated concentrations of ammonium and due to the toxic tendency of ammonia on nitrifying bacteria the process is inhibited [7]. It reported that 70% of ammonia from wastewater was removed using nitrification/ denitrification [8]. And, it reported the removal efficiency of ammonia by nitrification/denitrification was 87, 89, 72, 66 and 62%, at different concentrations of ammonia; 25, 40, 80, 120 and 160 mg/L [9]. Other researchers have employed algae for removing high concentration of ammonia from wastewater [10], the green algae *Scenedesmus sp.* was able to efficiently uptake ammonium in concentrations up to 100 mg/L. Halfhide et al. utilized microalgae to remove 65% of ammonia [11].

Due to the relatively slow of direct oxidation of ammonia by the ozone molecules, and also it produces nitrate that does not remove total nitrogen as well. It is reported a removal of 85% and 28.5% of ammonia and total nitrogen by ozonation, respectively [12, 13].

The exchange of similar charged ions from a liquid phase with ions electrostatically bound to an insoluble resin phase presents ion exchange process:

$$B^- + A \leftrightarrow B + A^- \qquad (2)$$

Modern synthetic ion exchange resins are polystyrene-divinylbenzene, sulfonic acid functional groups ($-SO_3H$) and zeolites (aluminosilicate minerals consist of SiO_4 and AlO_4) have exchange properties for 88%, 91.5% and 75-83%removing the positively charged ammonium ion [14-16].

Biosorption of pollutants is a very promising process in the removal of contaminants from wastewater. Moreover, it distinguished by its availabilities of sorbent substrates, economic effectiveness, the treatment plants are flexible in design and adsorbents can be regenerated by suitable desorption process. All of these characteristics make the biosorption to be aperient in the applications for removal of ammonia from environment [17-21]. Table (1) summarized all most reports on ammonium ions removal by adsorption method [22-35].

Table 1: The summary of reports on ammonium ions removal by adsorption method

Biosorbent	Maximum adsorption capacity (mg/g)	Removal %	References
Posidoniaoceanica (L.) fibers	1.8	-	22
Activated sludge	88	95	23
Microbacterium sp.	-	91.3	24
Supported Pt catalysts	-	97.5	25
Ozone	-	99	26
Ozone	0.44	-	27
Macro-algae	0.3	70	28
GAC-sand dualmedia filter	-	45	29
Novel acryl biofilm carrier material	-	98.5	30
Ammonia volatilization	-	99	31
Activated carbon	1.8	-	32
Modified chitosan	-	82.1	33
Zeolite synthesized from fly ash	24	-	34
Saw dust	1.7	-	35

In our contribution, the behavior of a low-cost adsorbent, water hyacinth, *Eichhornia Crassipes* leaves powder (ECLP), was employed to the removal of ammonia from synthetic and real drainage wastewater and determining the optimal operating conditions to obtain high efficiency of removal. Langmuir isotherm and Freundlich isotherm equations are an empirical adsorption models, were described to determine the adsorption capacity of *Eichhornia Crassipes.* The Langmuir and Freundlich equations were considered for determination of the equilibrium isotherms in terms of adsorption affinity and maximum adsorption capacity. The results indicated the Langmuir equation was well fitted the equilibrium adsorption proving monolayer adsorption.

2. Material and Methods

2.1. Materials

Ammonia stack solutions 25% produced by sigma Aldrich. Real wastewater sample was collected from Sabal drain, Menoufia, Egypt. HCl (1 M) and NaOH (1 M), were used for adjusting pH for desired values of synthetic and real samples were adjusted for desired value. Whatman qualitative No. 4, filter paper used for separation of the biosorbents from treated effluents.

2.2. Equipment

An adjustment of pH for the desired values of the suspensions is carried out utilizing WTW pH-meter, Germany. Lab shaker, SHO-2D, Korea was utilized for shaking wastewater samples which is in suspension with biosorbents, scanning electron microscope (SEM) images of the ECLP were taken at different magnifications using Quanta-250 FEG, USA. Utilizing Jasco-FTIR-Spectroscopy, Japan, FTIR spectra for adsorption of different function groups of the ECLP were recorded in the range of 350-4000 cm^{-1}.

2.3. Preparation of the biosorbent

Eichhornia Crassipes (Water hyacinth) leaves was collected from Rosetta branch of Nile River at Menoufia, Egypt; to remove dust, the collected plant were washed thoroughly using tap water and it followed by washing using deionized water and then, overnight drying of the plant samples were taken place in furnace at 80 ˚C, using a laboratory mill, the dried plant was grinded, then sieved and washed using deionized water and for *decolorization purposes, ECLP* rinsed with diluted HCl and then with diluted NaOH, finally, washed with deionized water many times for neutralization, and the last step was the drying process at 80 ˚C for 24 h and desiccated to be ready for the experiments.

2.4. Methodology

For batch method, using deionized water, fresh solutions of ammonia with known initial concentrations, were prepared. Before conducting the experiments, different prepared solutions were adjusted for desired pH values prior to conducting the treatment procedures. In suitable bottles, 100 ml of prepared solutions and different biosorbent doses were added and shaken well at 250 rpm using the lab shaker for the desired time (5-60 min.). The biosorbents were separated from water by filter paper. The American Standard Methods for examinations of water and wastewater was considered for measuring all parameters of raw and treated wastewater (APHA, 2017) [36]. Composite real wastewater were collected from Sabal drain and stored in ice box and transported to the laboratory, then it stored in refrigerator for analysis and treatments. According to techniques given in the American Standard Methods (APHA, 2017), all physico-chemical parameters of raw and treated real wastewaters have been analyzed [36].

3. Results and Discussions

3.1. Investigations of ECLP

SEM image of ECLP at high magnification shows the particle size of ECLP is ranged between ~ 2.44 - 55.7 μm as shown in Figure 1a and figure 1b exhibits the pore structure onto the surface of ECLP ~ (0.86 -2.29 μm. In general, SEM images show beside the porous distributions and their morphological structure along the surface of the ECLP, it also represents a good description of the particle size before adsorption studies. Figure 1c displays the FTIR spectrum of ECLP, abundant of active chemical sites were illustrated. The peak at 3854 cm^{-1}, 3746 cm^{-1} and 3493 cm^{-1} assigned to the O-H stretching vibrations, the peak at 2924 cm^{-1} assigned to the C-H stretching vibration, the peak at 1640 cm^{-1} assigned to C=C, while the peak at 1543 cm^{-1} assigned to the N-H bending, the peak at 1457 and 1427 cm^{-1} assigned to the O-H bending or the C=O group stretching, peaks at 1457 and 1427 cm^{-1} arise from identical C-H stretching, while the broad band from1036 cm^{-1} indicates the presence of C-O stretching, whereas the peaks at 623.8 cm^{-1} and 520.6 cm^{-1} engender due to C-halogen stretching. It was notified that most of these functional groups have capability to adsorb ammonia very well [37].

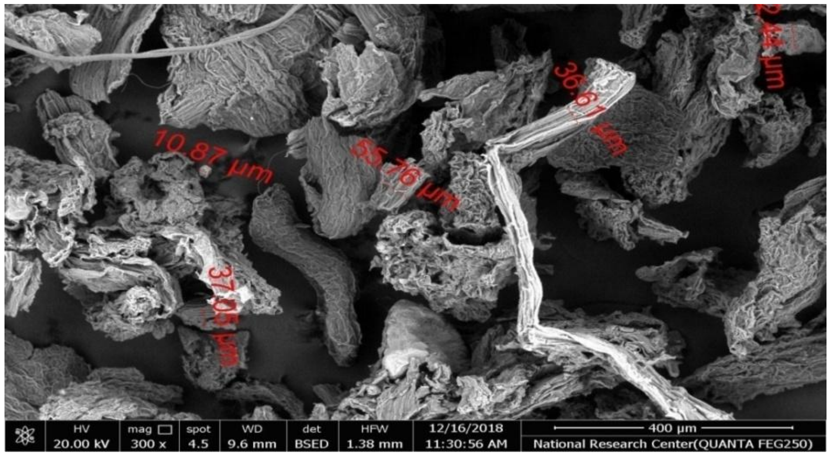

Figure 1a: showed the particle size of ECLP

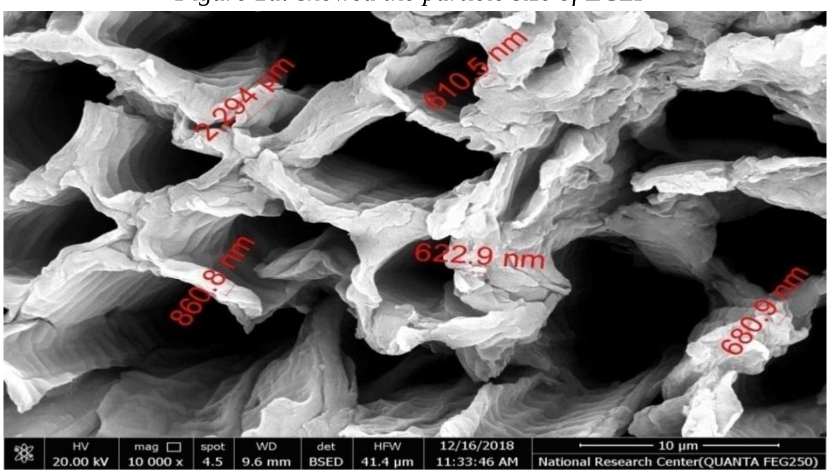

Figure 1b: showed the pore size at the surface of ECLP

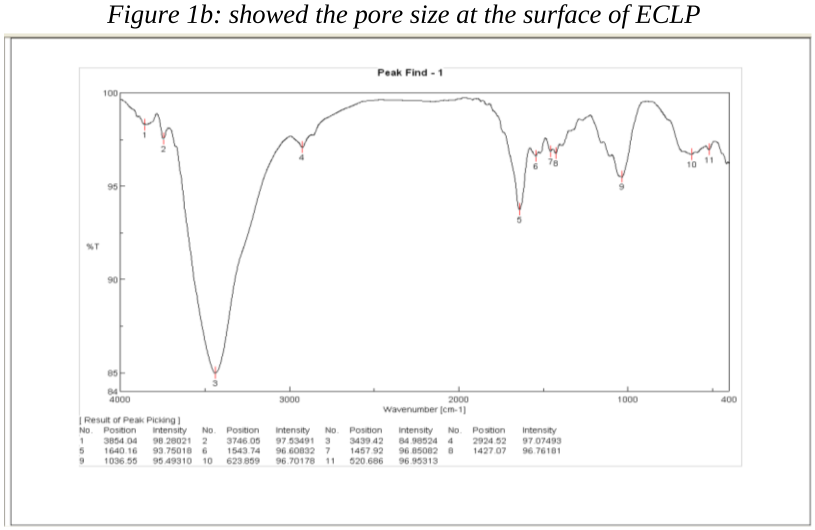

Figure 1c: FTIR spectrum of ECLP

3.1. Adsorption Investigations

Firstly, ammonia synthetic solution was employed for determining the optimum conditions at various parameters such as biosorbent doses ranged (1 - 5 g/L), the pH were adjusted to the desired values in the range between (3 - 9) at different contact time (5, 10, 20, 30, 40, 60 minute) and initial concentration of ammonia (3, 4, 6, 8, 10 mg/L) for high ECLP biosorption efficiency. The Langmuir and Freundlich equations were employed to determine the equilibrium isotherms in terms of adsorption affinity and maximum adsorption capacity. The treatment method was employed to treat real wastewater from Sabal drain at Menoufia, Egypt.

Different amounts of ECLP (0.5, 1, 2, 3, 4 and 5 g/L) were selected to find the optimal dose at constant nature pH (7.4), initial ammonia concentration (10 mg/L), shaking speed (250 rpm) and contact time (60 minutes). Figure (2a) showed that, with increasing of ECLP dose, ammonia percentage removal increased whereas Figure (2b) illustrated that, adsorption capacity or the uptake of ammonia was decreased with increasing ECLP content, these findings may attributed to the point of saturation of active sites of the biosorbent. The pH factor had a significant effect on the uptake of total ammonia by changing the pH values (3, 4, 5, 6, 7, 8 and 9) at the following conditions: biosorbent dose (5 g/L), initial concentration of ammonia (10 mg/L), shaking speed (250 rpm) and contact time (60 minutes) as shown in Figure 3; The uptake of the total ammonia impacted significantly with the pH of the solution. Figure 3 showed the maximum adsorption of ammonia was at pH ~5, it is matched with the results previously published [38]. The effect of contact time was studied at different intervals (5, 10, 20, 30, 40, 50 and 60 minutes) on the removal percentage of total ammonia over ECLP at constants (Figure 4): pH ~5, using a dose of biosorbent of 5 g/L, at 250 rpm of shaking and initial ammonia concentration of (10 mg/L); In the first 20 min, a rapid rate in uptake of ammonia was noticed due to the free cavities showed in Figure 1b, then become slowly until reach equilibrium at 40 minutes, which is comparable with the results previously published [38].

At equilibrium, ammonia removal percentage reached 88% which is more than the results previously published utilized microalgae for only 65% ammonia removal [11], the ammonia removal is used ozonation technology for removal of ammonia which reached only 28%, and comparable with the results obtained by Luo et al. (2015) [12] two-stage ozonation and the removal of ammonia reached 85% [12,13]. The behavior of ammonia uptake by ECLP were carried out using different initial ammonia concentrations (3, 4, 6, 8 and 10 mg/L) at optimum pH (5), dose of biosorbent (5 g/L) at 250 rpm shaking speed and contact time (40 minutes). Figure (5a) showed the percentage removal of ammonia decreased with increasing in its initial concentration, while with increasing ammonia concentrations, the amount of biosorbent concentration remained constant while the binding sites become more quickly saturated [39]. Figure (5b) show ammonia uptake increases with the increasing in its initial concentration.

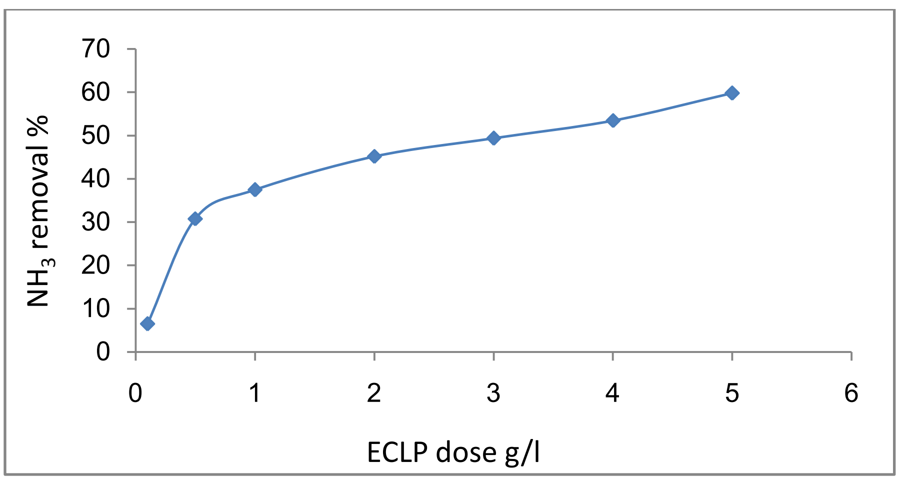

Figure 2a: Effect of ECLP dose on removal % of NH_3

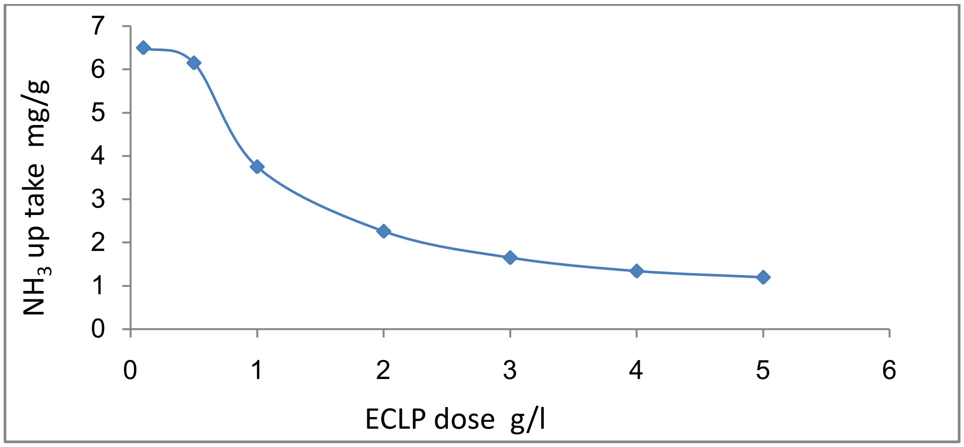

Figure 2b: Effect of ECLP dose on uptake of NH_3

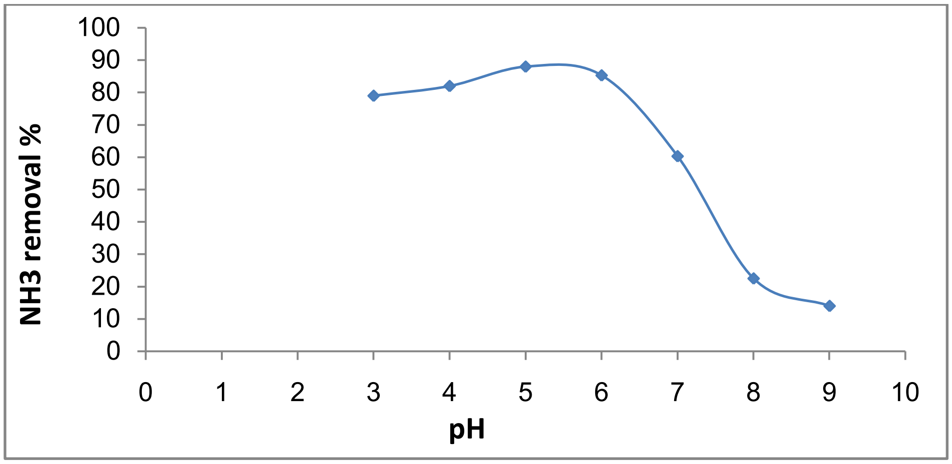

Figure 3: Effect of pH on NH_3 removal %

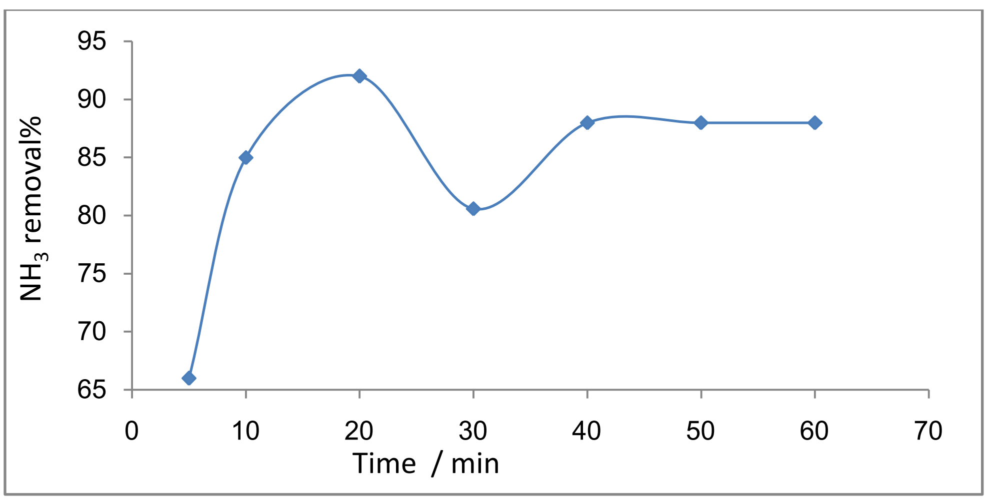

Figure 4: Effect of contact time on removal% of NH_3

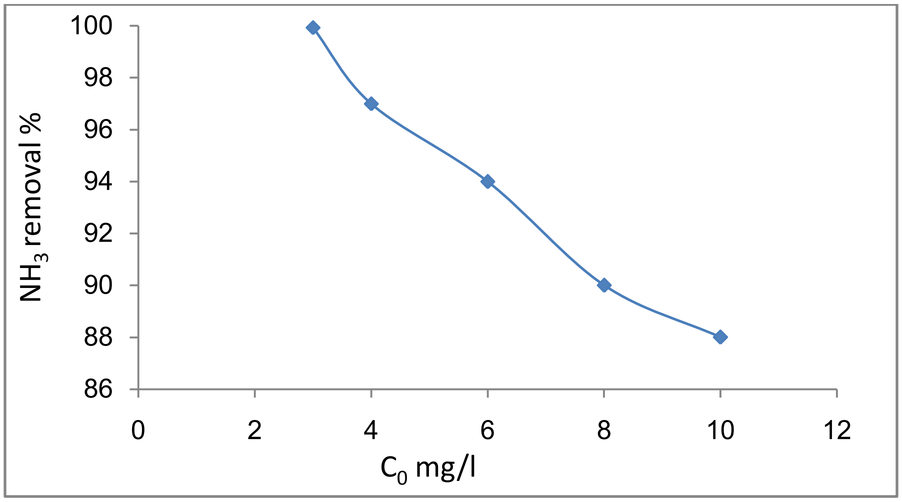

Figure 5a: Effect of initial concentration on removal of NH_3

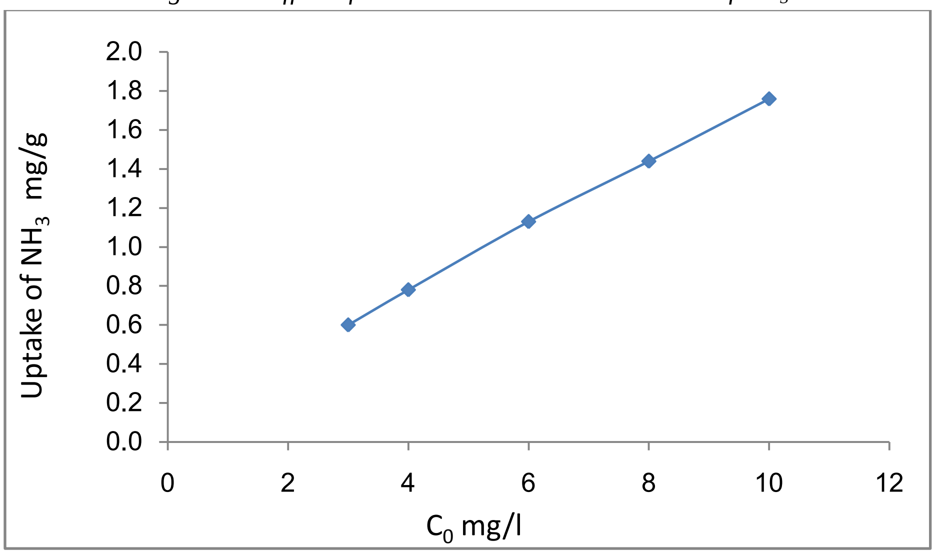

Figure 5b: Effect of initial concentration on NH_3 uptake

Adsorption isotherm

The relevant between the amount of solute adsorbed and the concentration of the solute in the aqueous phase is presented by adsorption isotherm equations. Evaluation of theses isotherms had been done in order to characterize the process of adsorption [40]. The adsorption isotherm equations, Langmuir and the Freundlich have been applied to many adsorption processes prosperity [41-45]. In this study, these isotherms will be adopted, as follows:

Langmuir isotherm equation

The Langmuir hypothesis based on the maximal adsorption affinity matched with the monolayer saturation of the solute on the surface of the adsorbent material at constant adsorption energy, there is no immigration of solute in its surface [46].

The equation of Langmuir isotherm is presented as:

$$q_e = \frac{q_{max} * K_l C_e}{1 + K_l C_e} \quad (3)$$

Linearized form is:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_l} + \frac{1}{q_m} * C_e \quad (4)$$

From equation (5)

$$\text{Slope} = \frac{1}{q_m} \quad (5)$$

$$\text{Intercept} = \frac{1}{q_m\ K_l} \quad (6)$$

q_m: Langmuir constants related to the sorption capacity, K_L: sorption energy, Ce: the concentration of solute at equilibrium in mg/L, q_e: the amount adsorbed of adsorbate per unit gram of adsorbent (mg/g), R_L: The equilibrium parameter of Langmuir dimensionless constant separation factor, is defined by the equation:

$$R_L = \frac{1}{1+K_L * C_e} \quad (7)$$

The value of R_L showed unfavorable when ($R_L>1$), linear when ($R_L=1$) but favorable when ($0 < R_L < 1$) and irreversible when ($R_L=0$). In our work, the adsorption process of ammonia with ECLP is favorable due to, the R_L-values are confined between 0 and 1. The massive values of K_L indicated strong binding between ammonia and the biosorbent [44-52]. Figure 5 showed a straight line of the plotted C_e/q_e against C_e. The related constants are: slope=0.555, intercept=0.063, R^2 = 0.965, K_L = 8.81, R_L= 0.011 - 0.036, and $q_{m=}$1.80.

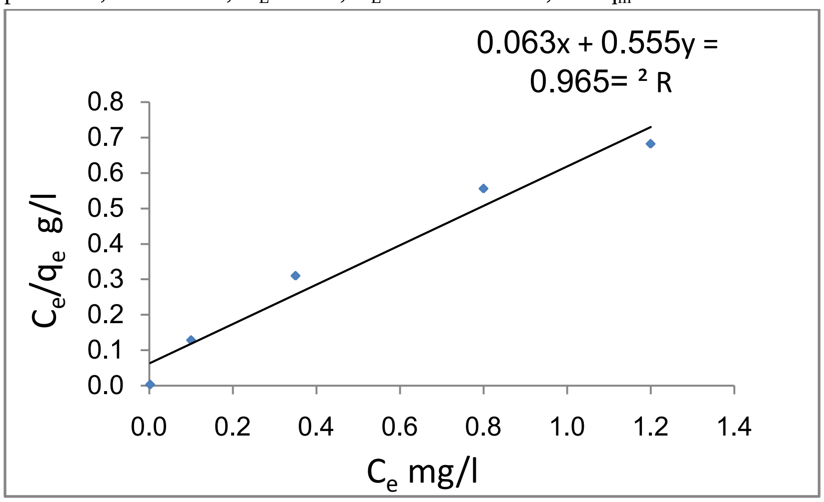

Figure 6: Langmuir plot of ECLP as adsorbent for NH_3 removal

Freundlich isotherm equation

This isotherm is a widely used mathematical description which gives a term involving the surface heterogeneity and the exponential distribution of the actively binding sites and their related energies [50,53].

The isotherm is presented as:

$$q_e = C_e^{\frac{1}{n}} \quad (8)$$

The linearized form is:

$$\ln q_e = \ln K_F + (\frac{1}{n}) \ln C_e \quad (9)$$

$$\text{Slope} = \frac{1}{n} \quad (10)$$

$$\text{Intercept} = \text{lin } K_F \quad (11)$$

Where C_e = concentration of adsorbate (ammonia) in the solution at equilibrium in mg/L, q_e = amount of adsorbate (ammonia) which adsorbed per unit weight of adsorbent (mg/g). "K_F" = parameter related to the temperature and "n" is a characteristic constant for the adsorption system under study, Figure 6 showed a straight line of the plots of (ln q_e) against (ln Ce); the values of "n" are confined between 2 and 10 which represented high adsorption characters (53). The isotherm constants are given as: slope = 0.157, intercept = 0.36, n = 6.37, Ln K_F =0.36, K_F =1.43 and R^2 = 0.857.

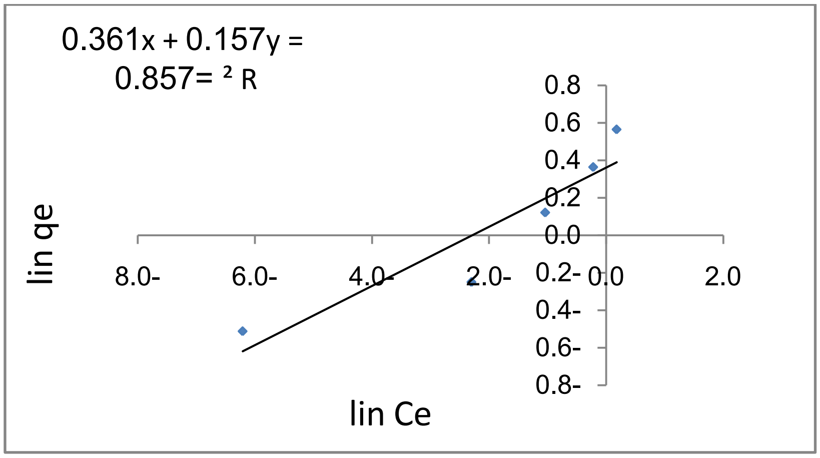

Figure 7: Plot of Freundlich isotherm for adsorption of NH_3 on ECLP

Case Study

The treatment procedures are applied to the drainage wastewater which was collected from Sabal canal, Menoufia, Egypt. The physico-chemical characterizations of the drainage wastewater as well as the treated effluents using ECLP are illustrated in (Table 2). Removal of COD, TDS, chloride, sulphate, ammonia, nitrates, nitrite, silica, iron, manganese, copper, zinc, aluminum and lead reached 75%, 98%, 96%, 83%, 87%, 95, 95%, 14%, 20%, 42%, 65%, 23%, 20%, 30% and 50% respectively. A complete removal of ammonia was reached when an extra addition of ECLP to the treated and filtered effluent, 1.2 g/L was needed dose. According to our pervious study, the construction and running costs of the treatment can be calculated proved that it is a low cost treatment [52], in comparison with the preceding studies, one study utilizing membrane technologies, they calculated a sum of 1.67 USD/m^3 of total cost, other researchers calculated the cost of 1.974 \$/m^3, they utilize the electro-oxidation reactor, our study presented a total cost ranged between 0.48 and 0.55 \$/m^3.

Table 2: Drainage wastewater analysis before and after treatment using ECLP

Parameter	Raw wastewater	Treated wastewater	% Removal
pH	7.6	7.4	--
COD, mg/L	358	89	75
Total dissolved solids, mg/L	880	17.8	97.9
Chloride, mg/L	260	10.8	95.8
Sulphate, mg/L	146	25	82.8
Ammonia, mg/L	7.1	0.9	87.3
Nitrates , mg/L	20.8	1.1	94.7
Nitrite , mg/L	0.4	0.02	95
Phosphate , mg/L	160	137	14.3
Silica , mg/L	0.5	0.4	20
Iron, mg/L	5.2	3	42.3
Manganese, mg/L	0.23	0.08	65
Copper, mg/L	0.26	0.2	23
Zinc , mg/L	0.05	0.04	20
Aluminum, mg/L	0.1	0.07	30
Lead, mg/L	0.1	0.05	50

Conclusions

The batch method was employed in the removal of ammonia from aqueous solution as well as real wastewater which was collected from Sabal drain, Menoufia, Egypt. the experiments carried out through utilizing of low cost adsorbent water hyacinth, *Eichhornia Crassipes* leaves powder (ECLP) which was collected also from Sabal drain. Optimizations of treatment parameters such as: pH, contact time, adsorption dose as well as the influence of the initial concentration of ammonia were achieved at ambient temperature 25±2 C˙. The results showed that, the higher (ECLP) doses, the higher ammonia removed, while the adsorption capacity is decreased. The optimum pH was 5±0.2 for the best removal of ammonia. The removal of ammonia is rapidly noticed at the first 20 minutes, while the equilibrium reached after 40 minutes. The separation factor of Langmuir constant, R_L, indicated the adsorption process of ammonia with ECLP is favorable due to, the R_L-values are confined between 0 and 1. Whereas, the massive values of K_L indicated strong binding between ammonia and the biosorbent. The Langmuir isotherm is better fitted than the Freundlich one, where, the correlation coefficient (R^2) for the Langmuir isotherm was higher than that of the Freundlich isotherm for the experimental results. In the case study, real drainage wastewater was collected from Sabal canal, Menoufia, Egypt., and subjected to the treatment processes utilizing the low-cost (ECLP), removal of COD, TDS, chloride, sulphate, ammonia, nitrates, nitrite, silica, iron, manganese, copper, zinc, aluminum and lead reached 75%, 98%, 96%, 83%, 87%, 95, 95%, 14%, 20%, 42%, 65%, 23%, 20%, 30% and 50% respectively. A complete removal of ammonia was reached when an extra addition of ECLP to the treated and filtrated effluent, a dose of 1.2 g/L was needed, our study offered a lowcost solution for removal of toxic ammonia from drainage wastewater for reuse, a total cost ranged between 0.48 and 0.55 $/m^3 that improved the cost effectiveness.

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